

Article

Synthesis, Characterization and Magnetic Studies of a Tetranuclear Manganese(II/IV) Compound Incorporating an Amino-Alcohol Derived Schiff Base

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Abstract: A new tetranuclear mixed-valence manganese(II/IV) compound $[\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}_3(\mu\text{-Cl})_3(\mu_3\text{-O})(\text{L})_3]$ (**1**) (where $\text{H}_3\text{L} = (3\text{E})\text{-3-}((\text{Z})\text{-4-hydroxy-4-phenylbut-3-en-2-ylideneamino})\text{propane-1,2-diol}$) has been synthesized and characterized by different physicochemical methods. Single crystal X-ray diffraction analysis reveals that **1** is a tetrahedral cluster consisting of a $\text{Mn}_4\text{Cl}_3\text{O}_4$ core in which the only Mn(II) ion is joined through three $\mu_2\text{-O}$ bridges to an equilateral triangle of Mn(IV) ions, which are connected by a $\mu_3\text{-O}$ and three $\mu_2\text{-Cl}$ bridges. The redox behavior of **1** was studied by cyclic voltammetry. Variable temperature magnetic susceptibility measurements of **1** revealed predominant antiferromagnetic coupling inside the $\text{Mn}_4\text{Cl}_3\text{O}_4$ cluster.

Keywords: tetranuclear cluster; manganese(II/IV); Schiff base; crystal structure; tetrahedral clusters; electrochemistry; antiferromagnetic coupling

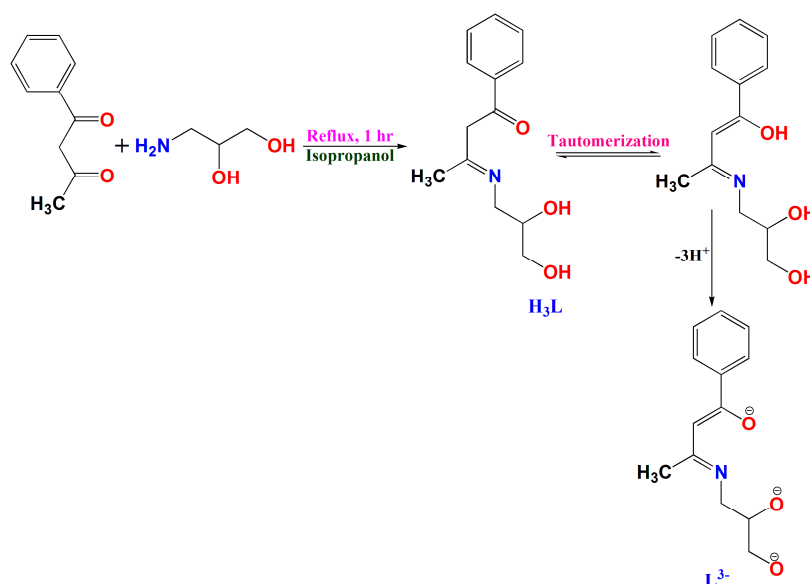
1. Introduction

Paramagnetic metal clusters are widely utilized in magnetic, electronic, optical, biological, and catalytic studies and applications [1,2]. Though researchers are engaged in the development of several synthetic strategies to design such complexes with high nuclearity, their synthesis is still challenging [3–5]. Polydentate ligands, functioning as chelators and bridges, are capable of coordinating with several metal centers and their pendant donating atoms can join other metal centers to construct various intricate structures [6,7]. Schiff bases derived from amino alcohols have proven to possess the ability to form polynuclear complexes [1,2], which play a significant role as biomimetic models of metalloproteins [8,9].

Catalytic and magnetic behaviors of many mixed-valence manganese complexes have been investigated using different synthetic strategies [4,10]. The most common oxidation state originates in these hetero-valence manganese complexes are Mn^{II} , Mn^{III} and Mn^{IV} [11–13]. Due to the presence of numerous possibilities in different magnetic coupling between pairs of ions in various oxidation states (II/II, II/III, II/IV, III/III, III/IV and IV/IV pairs), very high values of total molecular spin (S) [14–17] are an expected phenomenon in these complexes. The molecular magnetism of mixed-valence

tetranuclear manganese clusters has been explored, and has been examined as biomimetic models of PS II [1,2,14–16].

In this context, we have isolated a new mixed-valence manganese compound $[\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}_3(\mu\text{-Cl})_3(\mu_3\text{-O})(\text{L})_3]$ (**1**), incorporating a new Schiff base ligand H_3L ($\text{H}_3\text{L} = (3\text{E})\text{-3-}((\text{Z})\text{-4-hydroxy-4-phenylbut-3-en-2-ylideneamino})\text{propane-1,2-diol}$) (Scheme 1). The title compound has been characterized by micro-analytical analysis, FT-IR and UV/Visible spectroscopy, cyclic voltammetry and variable temperature magnetic measurements. The single crystal X-ray structure determination shows that **1** is a tetrahedral manganese cluster bearing a $\text{Mn}_4\text{Cl}_3\text{O}_4$ core. The bond valence sum analysis (BVS) reveals different valence states in the manganese centers, with one Mn(II) and three Mn(IV) ions. The electrochemical characterization of the complex reveals a two-step single electron redox process involving the Mn(IV) centers. Variable temperature magnetic susceptibility measurements show predominant antiferromagnetic intra-cluster coupling in compound **1**.



Scheme 1. Schematic diagram for the synthesis of the Schiff base (H_3L) and its deprotonated form (L^{3-}).

2. Results and Discussion

2.1. Discussion

Condensation of a mixture of equivalent amounts of Benzoyl acetone and 3-aminopropane-1,2-diol in methanol yield a new Schiff base ligand, ($\text{H}_3\text{L} = (3\text{E})\text{-3-}((\text{Z})\text{-4-hydroxy-4-phenylbut-3-en-2-ylideneamino})\text{propane-1,2-diol}$) (Scheme 1). A methanolic solution of H_3L was mixed with $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ and LiOH at a 1:1:1 ratio in isopropanol. The resulting solution was refluxed for an hour and the solvent subsequently removed by slow evaporation, which yielded red block shaped crystals of $[\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}_3(\mu\text{-Cl})_3(\mu_3\text{-O})(\text{L})_3]$ (**1**) after one week.

2.2. FT-IR Spectroscopy

The solid state FT-IR spectrum of H_3L and **1** is shown in the supplementary materials (Figure S1). These spectral studies reveal that the azomethine ($\nu_{\text{-CH=N-}}$) stretching frequency of the H_3L (1602 cm^{-1}) was shifted to a lower energy in the complex and appeared at 1591 cm^{-1} . The $\nu(\text{C}_{\text{alk}}\text{-O})$ stretching vibration of the H_3L (1270 cm^{-1}) was also moved to lower energies in the complex and appeared at 1112 cm^{-1} . The stretching vibration corresponding to aliphatic-OH ($\nu_{\text{-CH}_2\text{-OH}}$) of the H_3L (centered a 3305 cm^{-1}) was not observed in the spectrum of **1**, confirming its deprotonation upon complexation. The binding of the ligand was further substantiated by the presence of a number of bands in the range $412\text{--}567\text{ cm}^{-1}$, assignable to the Mn–O and Mn–N bonds [18].

2.3. Electronic Spectrum

Electronic absorption spectra of H_3L (Figure S2) and **1** (Figure 1) were recorded in acetonitrile at 300K. The free ligand showed two peaks at 242 and 372 nm, assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, which on chelation underwent red shift and appeared at 248 and 374 nm in the spectrum of **1**. An additional shoulder appeared at 473 nm in the spectrum of **1** that may be considered as a combination of ligand to metal charge transfer (LMCT) and ligand-field transitions involving the manganese(IV) ions. Weak d-d transition bands for Mn(IV) ions are found at 850 and 966 nm, corresponding to ${}^2T_{1g} \rightarrow {}^4A_{2g}$ and ${}^2E_g \rightarrow {}^4A_{2g}$ transitions, respectively [19].

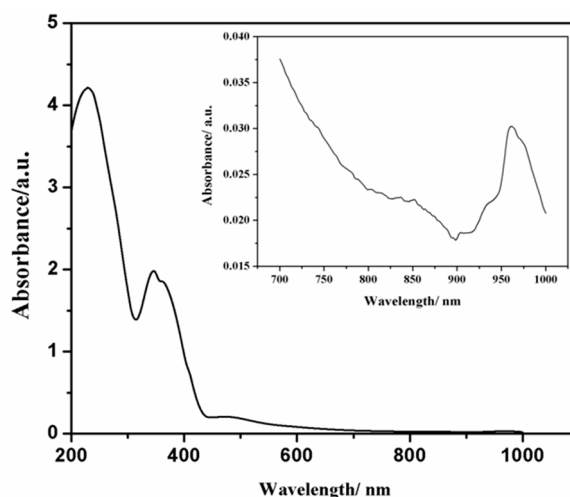


Figure 1. UV/Visible spectrum of **1**, recorded in acetonitrile at 300K. Inset: zoom of the high wavelength region showing the d-d band.

2.4. Crystal Structure Description

The single crystal X-ray diffraction study shows that compound **1** crystallizes in the trigonal space group $R\bar{3}$. Figure 2(left) shows a perspective view of **1** with atom labels. The compound possesses a tetra nuclear tetrahedral Mn_4 structure (Figure 2(right)). Relevant bond distances and angles of **1** are listed in Table 1.

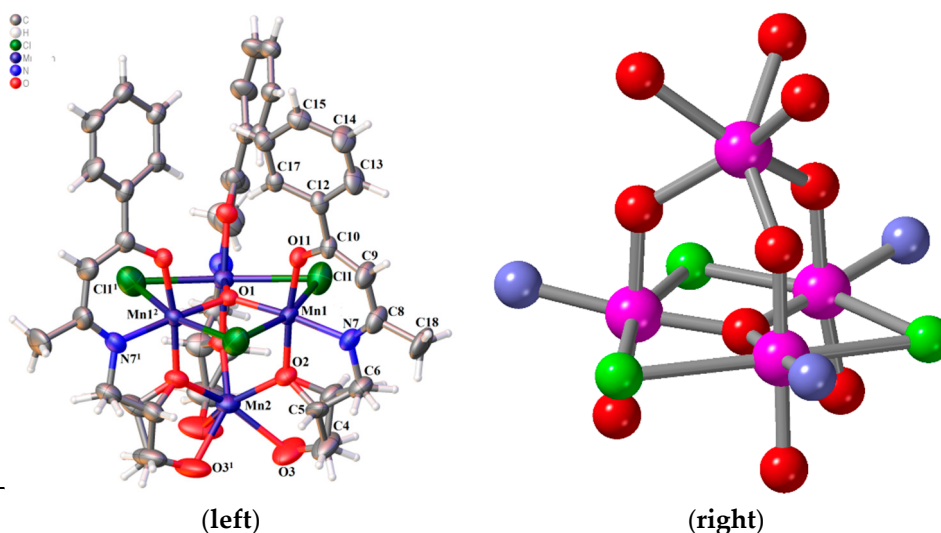


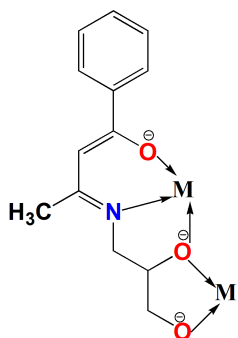
Figure 2. (left) Perspective view of the compound **1** with atom labels. (right) View of a tetrahedral Mn_4 core with coordinating atoms in compound **1**. Symmetry operations: ${}^1 = 1 - y, x - y, z$; ${}^2 = 1 + y - x, 1 - x, z$.

Table 1. Relevant bond distances (Å) and angles (°) for compound **1**.

Bond Lengths (Å)			
Mn1-Cl1	2.663(3)	Mn2-O2	2.134(5)
Mn1-O1	1.8873(11)	Mn2-O3	2.115(8)
Mn1-O2	1.892(5)	Mn2-O3	2.227(7)
Mn1-O11	1.890(4)	Mn2-O3 ¹	2.228(7)
Mn1-N7	1.984(6)		
Mn1-Cl1 ¹	2.719(3)		
Bond Angles (°)			
Cl1-Mn1-Cl1 ¹	164.90(8)	O2 ¹ -Mn2-O2	93.30(18)
O1-Mn1-Cl1	83.38(6)	O2 ¹ -Mn2-O3	147.6(4)
O1-Mn1-Cl1 ¹	81.83(7)	O2 ² -Mn2-O3	116.6(4)
O1-Mn1-O2	93.2(3)	O2-Mn2-O3	74.1(2)
O1-Mn1-O11	94.3(2)	O3 ² -Mn2-O3	85.0(3)
O1-Mn1-N7	174.7(3)	O3 ¹ -Mn2-O3	85.0(3)
O2-Mn1-Cl1	91.20(18)	O3 ² -Mn2-O3 ¹	85.0(3)
O2-Mn1-Cl1 ¹	92.64(17)	Mn1-Cl1-Mn1 ²	74.35(8)
O2-Mn1-N7	82.1(2)	Mn1 ¹ -O1-Mn1 ²	119.00(7)
O11-Mn1-Cl1	91.87(16)	Mn1-O2-Mn2	125.5(2)
O11-Mn1-Cl1 ¹	86.22(16)		
O11-Mn1-O2	172.2(2)		
O11-Mn1-N7	90.3(2)		
N7-Mn1-Cl1	99.1(2)		
N7-Mn1-Cl1 ¹	95.9(2)		

Symmetry operations: ¹ = 1 - y, x - y, z; ² = 1 - x + y, 1 - x, z.

The tetranuclear mixed-valence manganese compound has a C_3 symmetry and possesses a Mn(II) center (Mn2) on the C_3 axis, three crystallographically equivalent Mn(IV) centers (Mn1, Mn1¹ and Mn1²), three fully deprotonated crystallographically equivalent Schiff base ligands, three bridging Cl[−] ligands, and a central oxido anion connecting the three Mn(IV) centers located on the C_3 axis. The ligand L^{3−} exhibits a μ -bridging tetradentate coordination mode of the type O₃N (Scheme 2) and is coordinated to both types of Mn ions.

**Scheme 2.** Coordination modes of deprotonated Schiff base ligand L^{3−} with metal ion (M = Mn(IV) and M' = Mn(II)) in **1**.

Thus, each of the three crystallographically equivalent Schiff base anions coordinated to one of the three Mn(IV) metals in a tridentate O₂N meridional mode through its enolato oxygen (O11), the imine nitrogen (N7), and the internal alkoxido oxygen atom (O2). The distorted octahedral geometry of the Mn(IV) ions is completed by two of the three equivalent μ -bridging chlorido ligands (Cl1 and Cl1¹; symmetry code: ¹ = 1 - y, x - y, z) and the μ_3 -oxido ligand (O1). Mn2 is coordinated by the three Schiff base anions via their terminal (O3) and internal (O2) alkoxido oxygen atoms, giving rise to a slightly distorted trigonal prismatic geometry. The coordination geometry, analyzed by the program

SHAPE [20,21], confirms that of Mn1 adopts a distorted octahedral geometry whereas Mn2 displays a distorted trigonal prismatic geometry (Table 2). Each Mn(IV) is joined to the Mn(II) ion by the O2 atom with a Mn1–O2–Mn2 bond angle of $125.5(2)^\circ$. The three μ -bridging chlorido ligands connect two Mn(IV) atoms with a Mn1–Cl1–Mn1² (symmetry operation: $^2 = 1 - x + y, 1 - x, z$) bond angle of $74.20(9)^\circ$ and form an equilateral triangle as a result of the C_3 symmetry of the cluster. The oxido (O1) atom is located on the C_3 axis at the center of the triangle and connected with three Mn(IV) atoms with a Mn1¹–O1–Mn1² bond angle of $119.00(7)^\circ$. The central core can be described as a tetrahedral Mn₄ cluster formulated as Mn₄Cl₃O₄, in which a Mn(II) ion is associated with three μ_2 -O bridges to an equilateral triangle of Mn(IV) ions, which are connected by a μ_3 -O and three μ_2 -Cl bridges. The Mn(IV)–Mn(IV) and Mn(IV)–Mn(II) distances in the cluster are 3.2523(17) and 3.5801(17) Å, respectively. Crystal packing reveals that very weak non-classical intermolecular C–H...Cl hydrogen bonding between aromatic hydrogen (H13) and chloride ligand (Cl1) with bond dimension C13–H13...Cl1 = 3.742(13) Å leads to a 3D supramolecular structure in its solid state.

Table 2. Shape values for the five possible coordination geometries found for coordination number six in Mn1 and Mn2 in compound 1. The minimum values are indicated in bold.

Geometry	Symmetry	Mn1	Mn2
HP-6	D _{6h}	33.617	36.993
PPY-6	C _{5v}	25.913	18.084
OC-6	O _h	3.592	8.406
TPR-6	D _{3h}	14.942	2.205
JPPY-6	C _{5v}	28.178	22.087

HP-6 = Hexagon; PPY-6 = Pentagonal pyramid; OC-6 = Octahedron; TPR-6 = Trigonal prism; JPPY-6 = Johnson pentagonal pyramid J2.

Although there are hundreds of discrete multinuclear Mn cluster compounds with oxido and/or chlorido bridges, the Cambridge Crystallographic Data Center CCDC search showed that compound 1 is the first structurally characterized tetranuclear Mn cluster with an Mn^{IV}₃Mn^{II}Cl₃O₄ core involving Mn(II) and Mn(IV) ions. Although there is a similar tetranuclear cluster formulated as [Mn^{III}₃Mn^{II}NaOCl₄(HL¹)₃]·3MeCN (HL¹ = 2-((E)-(2,3-dihydroxypropylimino)methyl)phenol, CCDC code: LIQXOA), it contains one Mn(II) and three Mn(III) ions, along with a Na⁺ cation connecting three Mn(III) atoms with a terminal Cl[−] ligand connected to the Na⁺ ion [22]. Additionally, there are two structures [Na₂Mn₇(μ₄-O)₂{μ₃-C₉H₇NO₂Ph(OMe)-κ¹-N,κ⁵-O,O',O''}₆(μ₂-Cl)₆]·CH₃OH·CH₃CN (C₉H₇NO₂Ph(OMe) = R-2-((E)-(2-hydroxy-2-phenylethylimino)methyl)-6-methoxyphenol, CCDC code: WAWRIY) and [Na₂Mn₇(μ₄-O)₂{μ₃-C₉H₇NO₂Ph(OMe)-κ¹-N,κ⁵-O,O',O''}₆(μ₂-Cl)₆]·CH₃OH·H₂O (C₉H₇NO₂Ph(OMe) = R-2-((E)-(2-hydroxy-2-phenylethylimino)methyl)-6-methoxyphenol, CCDC code: WAWROE) containing a cluster formed by two NaMn₄Cl₃O₄ clusters (along with one Mn(II) and three Mn(III), similar to LIQXOA) sharing a vertex to generate a sandglass shaped cluster of the type NaMn₃Cl₃O₄-Mn-Cl₃O₄Mn₃Na [23]. Finally, there are also two compounds, Na[Mn₈Na₂(μ₄-O){μ₃-C₉H₇NO₂Ph(OMe)-κ¹-N,κ⁵-O,O',O''}₆(μ₃-O)(μ₂-Cl)₉]·CH₃OH·H₂O (C₉H₇NO₂Ph(OMe) = 2-((E)-(2-hydroxy-2-phenylethylimino)methyl)-6-methoxyphenol, CCDC code: YEMBOK) and Na[Mn₈Na₂(μ₄-O){μ₃-C₉H₇NO₂(Prⁱ)(OMe)-κ¹-N,κ⁵-O,O',O''}₆(μ₃-O)(μ₂-Cl)₉]·CH₃OH·H₂O (C₉H₇NO₂(Prⁱ)(OMe) = 2-((E)-(2-hydroxy-3-methylbutylimino)methyl)-6-methoxyphenol, CCDC code: YEMBUQ) with a central cluster formed by two Mn₄Cl₃O₄ cores, again with one Mn(II) ion and three Mn(III) ions, which are connected by a triple μ-Cl bridge through the two equilateral triangular faces [24]. Mn(IV)–Cl distances in the range 2.663(3)–2.719(3) Å observed in 1 are slightly higher in comparison to the Mn(III)–Cl distances found in the range 2.631(5)–2.712(3) Å for the reported mixed valence manganese complex (YEMBOK) [1] with a Mn^{II}Mn^{III}₃(μ-Cl)₃(μ₃-O) triangular planar core. This can be attributed to the weak overlap between the Mn(IV) and Cl atom in the present compound, which probably arises due to the greater Mn(IV) ... Mn(IV) separation (3.2523 (17) Å) within the Mn^{IV}₃ triangular core in comparison the reported complex (YEMBOK), where Mn(III) ... Mn(III) separation

within the Mn^{III}_3 core are 3.252(1) and 3.248(2) Å. However, no such structure was found in CCDC bearing a similar core involving Mn^{II} and Mn^{IV} atoms.

The oxidation state of the manganese ions has been determined by the bond valence sum (BVS) calculation based on the correlation between bond valence and bond distance. Here, valence between the two atoms i and j can be calculated using the empirical formula [25,26].

$$S_{ij} = \exp(R_0 - R_{ij})/b \quad (1)$$

where bond valence between two atoms i and j is represented by the term S_{ij} . The observed bond length between i and j is symbolized by the term R_{ij} . R_0 and b are the tabulated bond valence parameters defined by Liu et al. [25]. The algebraic sum of S_{ij} values of all the bonds (n) around an atom i gives the oxidation number of the atom i and is symbolized by N_{ij} , which is given by the equation

$$N_{ij} = \sum S_{ij} \quad (2)$$

With this equation, the values obtained for compound **1** are $\text{Mn1}/\text{Mn1}^1/\text{Mn1}^2 = 4.224$ and $\text{Mn2} = 2.208$, which clearly confirms the oxidation states of both types of manganese center.

2.5. Electrochemistry

Figure 3 represents the cyclic voltammograms of compound **1**, measured within the potential range -2.0 to $+2.0$ V using $^n\text{Bu}_4\text{NClO}_4$ as the supporting electrolyte at the following scan rates: 50, 100, 150 and 200 mV s^{-1} . In the redox process, the tetranuclear compound **1** underwent two one-electron charge transfers, namely, (a) $\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}} \leftrightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ and (b) $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}} \leftrightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$. In the cathodic scan, the first peak, assigned to the $\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ reduction, appeared at 408, 386, 386 and 375 mV, vs. saturated calomel electrode (SCE), for the scan rates 50, 100, 150 and 200 mV s^{-1} , respectively. A second cathodic peak, attributed to the $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$ reduction, was observed at -328 , -369 , -414 and -458 mV vs. SCE, for the scan rates 50, 100, 150 and 200 mV s^{-1} , respectively. The anodic scan showed one oxidation peak, attributed to the $\text{Mn}^{\text{II}}\text{Mn}^{\text{II}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ oxidation, at -639 , -561 , -539 and -520 mV, vs. SCE, for the same respective scan rates [27,28]. The reversibility of the redox processes is supported by the difference in the respective reduction to oxidation peaks which were found to be 311, 192, 125 and 69 mV when measured at scan rates: 50, 100, 150, 200 mV s^{-1} , respectively. It was also found that with the increase of scan rate, the corresponding cathodic peak shifted to more negative values while the anodic peak shifted to more positive values with an increase of peak currents for both scans and, as a result, the $I_{\text{pc}}/I_{\text{pa}}$ being greater than 1, which also confirms the irreversible nature of the redox processes [28].

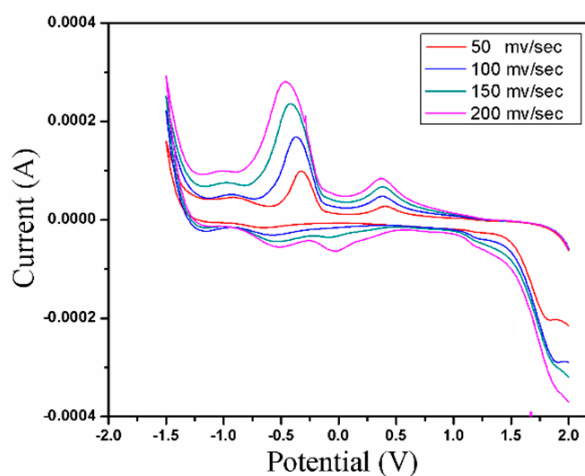


Figure 3. Cyclic voltammograms of compound **1** plotted at scan rates of 50, 100, 150 and 200 mV s^{-1} .

2.6. Magnetic Study

The thermal variation of the molar magnetic susceptibility per manganese tetramer times the temperature ($\chi_m T$) for compound **1** gives a room temperature value of ca. $10.9 \text{ cm}^3 \text{ K mol}^{-1}$, which is a little above the expected value for three independent $S = 3/2$ manganese(IV) ions and one $S = 5/2$ manganese(II) ion. On cooling, $\chi_m T$ shows a gradual decrease already observed at room temperature and reaches a minimum value of ca. $7.0 \text{ cm}^3 \text{ K mol}^{-1}$ at ca. 37 K (Figure 4). Below this temperature, $\chi_m T$ rises and reaches a maximum of ca. $8.7 \text{ cm}^3 \text{ K mol}^{-1}$ at ca. 5 K. Below ca. 5 K, $\chi_m T$ sharply decreases and reaches a value of ca. $8.1 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. This behavior suggests that the predominant interaction inside the Mn_4 cluster is antiferromagnetic, as shown by the continuous decrease of $\chi_m T$, starting from room temperature to ca. 37 K. Since there are two different exchange coupling constants inside the Mn_4 tetrahedron, if both are antiferromagnetic then they are expected to give rise to spin frustration, as not all pairwise interactions can present an antiferromagnetic interaction (see below). This spin frustration results in an intermediate spin ground state that gives rise to the observed increase of the magnetic moment below ca. 37 K. Finally, the decrease observed at very low temperatures can be attributed to the presence of a zero field splitting of the spin ground state and/or to the presence of weak antiferromagnetic inter-cluster coupling. The structure of the $\text{Mn}_4\text{Cl}_3\text{O}_4$ cluster in **1** shows that the manganese(II) ion is connected to another three manganese(IV) ions, and that there are two crystallographically independent manganese ions (three Mn1 atoms, corresponding to $S = 3/2$ manganese(IV) ions and one Mn2 atom, which is a $S = 5/2$ manganese(II) ion). A close look at the structure of the cluster also shows that there are two different exchange pathways (J_1 , connecting the three Mn1 ions through a μ_3 -oxido and a μ -chlorido bridge; and J_2 , connecting the Mn2 ion with the three Mn1 ions through a single μ -oxido bridge; see inset in Figure 4). Accordingly, we have used a model that takes into account the magnetic exchange scheme displayed in the inset in Figure 4 using the package MAGPACK [29,30] with the Hamiltonian $H = -J_1[S_2S_3 + S_2S_4 + S_3S_4] - J_2[S_1S_2 + S_1S_3 + S_1S_4]$. This model very satisfactorily reproduces the magnetic properties of complex **1** above the maximum at ca. 5 K with $g = 2.013$, $J_1 = -3.8 \text{ cm}^{-1}$ and $J_2 = -10.3 \text{ cm}^{-1}$ (solid line in Figure 4).

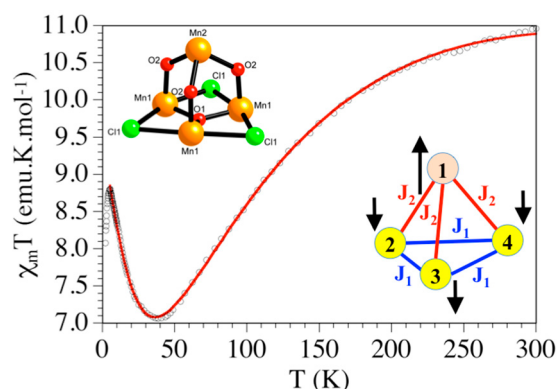


Figure 4. $\chi_m T$ (per Mn_4 cluster) vs. T plot for compound **1**. Solid line indicates the best fit to the tetramer model (see text). Inset shows exchange scheme of the Mn_4 cluster.

The observed two weak antiferromagnetic exchange interactions inside the Mn_4 tetramer leads to spin frustration. Thus, the stronger antiferromagnetic J_2 coupling constant implies that the spins of the Mn2 ions must be antiparallel to the three Mn1 ions. Therefore, the spins of the three Mn1 ions should be parallel to each other, in conflict with the antiferromagnetic coupling observed for J_1 .

Finally, the weak couplings found for both exchange interactions are in agreement to those observed for other oxido-bridged Mn clusters and can be explained from previous magneto structural correlations that indicate that the coupling in this kind of Mn cluster with single μ -oxido bridges is weak and antiferromagnetic [31–33]. Unfortunately, the few related $\text{Mn}_4\text{Cl}_3\text{O}$ clusters reported to date

contain one Mn(II) and three Mn(III) ions and the magnetic couplings, although usually weak and antiferromagnetic, cannot be compared with those of **1** [22–24].

3. Materials and Methods

3.1. Starting Materials

All solvents and chemicals used in the synthesis were of analytical grade. Benzoyl acetone and 3-aminopropane-1,2-diol were received from Aldrich Chemical Co. Inc. (Sigma-Aldrich, St. Louis, MO, USA). $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ and LiOH were obtained from E. Merck, India.

3.2. Syntheses

3.2.1. Synthesis of ((3E)-3-((Z)-4-hydroxy-4-phenylbut-3-en-2-ylideneamino)propane-1,2-diol)

The Schiff base (H_3L) was synthesized by reflux condensation of benzoyl acetone (0.162 g, 1 mmol) and 3-aminopropane-1,2-diol (0.091 g, 1 mmol) in 20 mL of methanol for an hour (Scheme 1). Pale yellow crystals of the ligand were obtained upon slow evaporation of the resulting solution. This was dried and stored in vacuo over CaCl_2 for future use. Yield: 0.185 g (82%). $\text{C}_{14}\text{H}_{21}\text{NO}_3$ ($M = 251.32 \text{ g mol}^{-1}$): Calculated: C, 66.91; H, 8.42; N, 5.57%. Found: C, 66.85; H, 8.37; N, 5.52%. FT-IR (cm^{-1}): 3305s, 2940w, 2866vw, 1834vw, 1602s, 1536s, 1438w, 1328w, 1270s, 1046s, 929w, 838w, 755w, 713w, 672w, 555w, 480w. UV/Vis (nm): 242 ($\pi \rightarrow \pi^*$), 372 ($n \rightarrow \pi^*$). ^1H NMR (CDCl_3 , 300 MHz) δ : 2.01 (s, 3H, $-\text{CH}_3$), 3.35–3.47 (m, 3H, NCH_2 , $-\text{OH}$), 3.61–3.73 (m, 3H, $-\text{OCH}_2$, OH), 3.95 (s, 1H, $\text{O}-\text{CH}$), 5.65 (s, 1H, Vinylic- OH), 7.36–7.41 (m, 3H, Ar-H), 7.80 (d, $J = 4.80 \text{ Hz}$, 2H, Ar-H), 11.46 (s, 1H, $-\text{OH}$) ppm (Figure S3).

3.2.2. Synthesis of $[\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}_3(\mu\text{-Cl})_3(\mu_3\text{-O})(\text{L})_3] (\mathbf{1})$

A methanolic solution (20 mL) of H_3L (0.239 g, 1 mmol) was added slowly to a warm isopropanolic solution (10 mL) of $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ (0.197 g, 1 mmol). Solid LiOH (0.041 g, 1 mmol) was added to the mixture. The resulting brown solution was refluxed for an hour, resulting in a darkening of the solution. The solution was cooled and filtered. Slow evaporation of the solvent yielded X-ray diffraction quality red block shaped single crystals of **1** within a week. Yield: 65%. $\text{C}_{39}\text{H}_{42}\text{Cl}_3\text{Mn}_4\text{N}_3\text{O}_{10}$ ($M = 1038.87 \text{ g mol}^{-1}$): Calculated: C, 45.09; H, 4.07; N, 4.04%. Found: C, 45.07; H, 4.03; N, 4.02%. FT-IR (cm^{-1}): 3413s, 2936w, 1591s, 1570m, 1543w, 1512vs, 1487s, 1453s, 1439m, 1432m, 1395s, 1364w, 1299s, 1254w, 1215w, 1187vw, 1159vw, 1112s, 1073w, 1028s, 940s, 911m, 880w, 855w, 799vw, 772s, 704s, 679w, 647vw, 603m, 567w, 530w, 481w, 421w, 412w. UV/Vis (nm): 248 ($\pi \rightarrow \pi^*$), 374 ($n \rightarrow \pi^*$), 473 (LMCT/LFT), 850 ($^2\text{T}_{1g} \rightarrow ^4\text{A}_{2g}$) and 966 nm ($^2\text{E}_g \rightarrow ^4\text{A}_{2g}$).

3.3. Physical Measurements

Elemental analyses (carbon, hydrogen, and nitrogen) were performed in a Perkin Elmer 2400 II elemental analyzer. The FT-IR spectrum of H_3L and **1** were recorded on a Perkin Elmer Spectrum RX I FT-IR system using a KBr pellet in the range 4000–400 cm^{-1} . The UV/Visible spectra of the H_3L and compound **1** were recorded on a Perkin Elmer Lambda 40 UV/Vis spectrometer using HPLC grade acetonitrile in the range 200–1100 nm. Proton nuclear magnetic resonance spectrum of H_3L was recorded in CDCl_3 on a 300 MHz Bruker Fourier transform NMR spectrometer using $(\text{CH}_3)_4\text{Si}(\text{TMS})$ as internal standard. Electrochemical studies of compound **1** were carried out on a PAR VersaStat-potentiostat/Galvanostat II electrochemical analysis system using conventional three-electrode configurations in acetonitrile with $^n\text{Bu}_4\text{NClO}_4$ as the supporting electrolyte in dry argon atmosphere. Cyclic voltammetry was performed at scan rates of $\nu = 50, 100, 150$ and 200 mV s^{-1} using platinized platinum millielectrode and saturated calomel electrode (SCE) as working and reference electrodes, respectively, along with a platinum counter electrode. Magnetic susceptibility measurements of polycrystalline sample of compound **1** (with a mass of 44.76 mg) were performed in the temperature range 2–300 K with an applied magnetic field of 0.1 T on a Quantum Design

MPMS-XL-5 SQUID susceptometer. The susceptibility data were corrected for the sample holders previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascal's constant tables ($\chi_{\text{dia}} = -545.43 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) [34].

3.4. X-ray Crystallography

A red block-shaped X-ray diffraction quality single crystal of compound **1** was mounted on fine glass fiber and placed on a Bruker Apex2 CCD area detector diffractometer equipped with a graphite monochromated fine focus Mo-K α ($\lambda = 0.7173 \text{ \AA}$) sealed tube. Crystal data of compound **1** were collected using Apex2 (Bruker, 2011) software at a temperature of 100 K using φ and ω scans. Absorption correction on the collected data was performed by Multi-scan SADABS2008/1 (Bruker, 2008). $R(\text{int})$ was 0.0620 before and 0.0513 after correction. Further details are given in Supplementary Materials (Table S1). The crystal structure of compound **1** was solved employing Olex2 [35], with the SHELXS [36] structure solution program using Direct Methods and refined with the SHELXL [37] utilizing least Squares minimization. The anisotropic displacement parameters were refined successfully for all non-hydrogen atoms. For hydrogen atoms of the aromatic rings and the imino groups, the corresponding hydrogen atoms were placed geometrically and refined using isotropic displacement parameters. The molecular pictorial representations and crystallographic illustrations were made by OLEX2 [35]. There was unresolved solvent, which was probably a mixture of isopropanol and methanol. Attempts at modelling were made but no chemically sensible distances were found from the residual electron density and attempts at squeezing out the solvent were unsuccessful since it was close to the main molecule (in particular the Cl ligand). The supplementary crystallographic data for **1**, $[\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}_3(\mu\text{-Cl})_3(\mu_3\text{-O})(\text{L})_3](\text{CCDC-1876188})$ is available free of charge via www.ccdc.cam.ac.uk/data_request/cif.

4. Conclusions

A new tetranuclear tetrahedral-shaped mixed valence manganese(II/IV) complex based on a bridging tetradentate Schiff base has been synthesized and characterized by spectroscopic methods. Single crystal X-ray diffraction studies reveal that Mn(IV) ions adopt a distorted octahedral geometry whereas the Mn(II) ion displays a slightly distorted trigonal prismatic geometry. The Mn(IV) ions embraced by three μ -chlorido and a single μ_3 -oxido bridge in a triangular plane are connected with the Mn(II) ion at the apex through endogenic μ -alkoxido bridges, resulting in a $\text{Mn}_4\text{Cl}_3\text{O}_4$ core. The magnetic susceptibility study shows a weak antiferromagnetic coupling inside the $\text{Mn}_4\text{Cl}_3\text{O}_4$ core of this tetrameric cluster compound.

Supplementary Materials: The following supplementary data are available online. Figure S1: IR spectra of H_3L and **1**. Figure S2: Electronic spectra of H_3L . Figure S3: ^1H NMR spectrum of H_3L . Table S1: Crystallographic information and structure refinement parameters for **1**.

Author Contributions: M.N. and S.S. planned and designed the experiments; M.N. performed the syntheses and carried out micro-analytical and spectroscopic characterization; G.R. performed crystallographic measurements and characterization; C.J.G.-G. carried out the magnetic studies; M.N. and S.S. wrote the paper.

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